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Hydrogen storage properties of Mg-doped $Ti_{1.2}Fe$ alloys synthesized by mechanical alloying①

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Abstract: Hydrogen storage properties and phase components of Mg-doped TiFe alloys, that were prepared by Ti, Fe and Mg metal powders using a mechanical alloying technique, were studied. XRD analyses show that the main phase of all the Mg-doped $Ti_{1.2}Fe$ alloys is the TiFe phase. Some $TiFe_2$ phase and α-Ti phase exist as secondary phases and Mg is dispersed in the alloy matrix. 3% Mg-doped and 5% Mg-doped $Ti_{1.2}Fe$ alloy samples can be fully activated within three hydriding/dehydriding cycles at room temperature and the hydrogen storage capacities of the alloys can reach 222 mL/g and 198 mL/g, respectively. Both two samples exhibit only one plateau region in their *P-C-T* curves with a low hydrogen absorption/desorption pressure hysteresis. The effect and mechanism of Mg addition as well as overstoichiometric Ti on the activation properties and hydrogen storage capacities of the alloys was also discussed.

Key words: TiFe alloy; Mg; hydrogen storage properties; mechanical alloying
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1 INTRODUCTION

Hydrogen storage materials, used in hydrogen source systems for fuel cells have been investigated due to their high volumetric density, safety, easy miniaturization and convenient operation. Considering all kinds of hydrogen alloys as a whole, AB-type TiFe alloys are known to be much more suitable for using in portable or mobile PEMFC because of its high reversible hydrogen storage capacity, which is much higher than that of AB_5-type alloys. On the other hand, the activation properties of the TiFe alloys are poor. For example, typically, such alloys need to be submitted to 10 hydriding/dehydriding cycles at temperatures higher than 673 K to be activated[1]. Research works tending to improve their activation kinetics have been carried out in a wide range of experimental conditions, such as partial substitution of Fe side of TiFe by transition elements Mn, Cr, V, Zr, Co, Ni etc.[2-5], adding small quantities of metallic elements[6, 7] or nonmetallic elements[8] in TiFe or overstoichiometric Ti side of TiFe[9]. Most of such modifications gave good results for activating TiFe alloys. However, in most cases, the alloys showed the common decrease of hydrogen absorption/desorption capacities and increased hysteresis and sloping of the pressure plateau properties.

Mg is a low density metal with a high absorption hydrogen rate within the ⅡA group in the element periodic table. It is known that Mg does not dissolve in Ti and Fe. Our previous work discussed the V-based multi-phase alloys, in which the activation properties of the alloys showed the remarkable improvement by the mechanical alloying (MA) synthesizing method and adding some easily hydriding alloys[10]. The addition of high hydrogen absorption capacity Mg may improve the activation properties of TiFe, and it is expected that the composite alloys would display good activation properties with a low capacity decrease. The present work deals with the hydrogen storage properties of Mg-doped $Ti_{1.2}Fe$ alloys prepared by MA.

2 EXPERIMENTAL

The chemical compositions of the alloys were designed as $Ti_{1.2}Fe+ x$ Mg (x = 1%, 3%, 5%), in which Ti component in TiFe compound is overstoichiometric. The purity of the component metals Ti, Fe and Mg was 99.5 %, 99.5 % and 99.9 %, respectively. The samples, according to the chemical compositions above, were prepared by mechanical alloying in a ball-milled machine. Each mixture was finished in a 100 mL vial with 1∶30 powder-to-ball

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mass ratio. The particle size of the raw materials was below 74 μm. Initially, the vial with the raw materials was evacuated. Then, high purity argon was charged up to 0.5 MPa. The rotating speed was kept at 225 r/min and the milling time was 60 h. After ball milling, the samples were transferred quickly into a reactor and submitted to the hydrogen absorption/desorption test.

The activation properties of the sample alloys were measured using a Sievert's type apparatus at room temperature. Sample powders of 5 g were loaded into a reactor, which was evacuated to 0.1 Pa and then charged with hydrogen up to 6.0 MPa. The pressure change, which was continuously monitored by a sensitive pressure transducer, was used to determine the rate of hydrogen absorption during the hydriding process. After maintaining the hydrogen pressure constant for a period of time, the hydrogen was released and the reactor was again evacuated to 0.1 Pa. Full activation of the samples was achieved by submitting them to several cycles; then, the pressure-composition isotherms at different temperatures were plotted.

The results of the X-ray diffraction (XRD) analyses of the samples were determined on a Philips X-rays diffractometer (X' Pert-MPD) with Cu K_α radiation. The range of the scanning angle (2θ) was 25°–85° and the scanning rate was 0.05(°)/s. The microstructures were examined on a Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS).

3 RESULTS AND DISCUSSION

3.1 Activation properties of $Ti_{1.2}Fe + x$ Mg (x = 1%, 3%, 5%) alloys

Fig. 1 shows the first hydriding curve of $Ti_{1.2}Fe + x$ Mg (x = 1%, 3%, 5%) alloys prepared by MA at room temperature under 6.0 MPa of initial hydrogen pressure. Each alloy with three different Mg-doped contents shows good hydrogen absorption properties even without activation pretreatment. For x = 1%, the incubation period of the alloy is about 20 min and for x = 3% and 5% no obvious incubation periods can be observed in the hydriding processes. For these three sample alloys, the alloy with x = 3% shows the fastest hydriding rate and the highest hydrogen storage capacity. Hydriding curves of $Ti_{1.2}Fe$ + 3% Mg alloys with different cycles are shown in Fig. 2. From Fig. 2, it can be seen that the hydriding curve for the third cycle approaches that for the tenth, which indicates that the alloys are fully activated within three absorption/desorption cycles. Comparison of the capacity after the first cycle to that for the following cycles that display lower capacity shows that some stable hydrides are formed during the first hydriding cycle. It is believed that Mg and overstoichiometric Ti had preferential to absorb hydrogen at the first contact of the alloys and hydrogen. During the formation of irreversible Mg and Ti metal hydrides, volume expansion occurs inducing the creation of micro-cracks in the TiFe matrix, and then establishing a highly active TiFe surface.

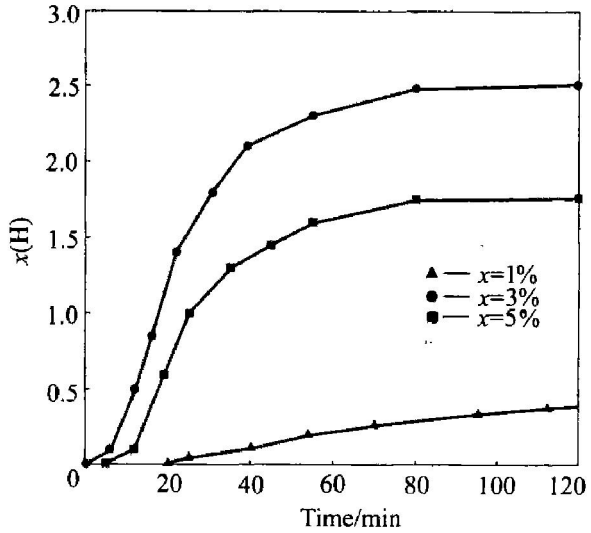

Fig. 1 Initial hydriding curves of $Ti_{1.2}Fe + x$ Mg (x = 1%, 3%, 5%) alloys at room temperature under 6.0 MPa

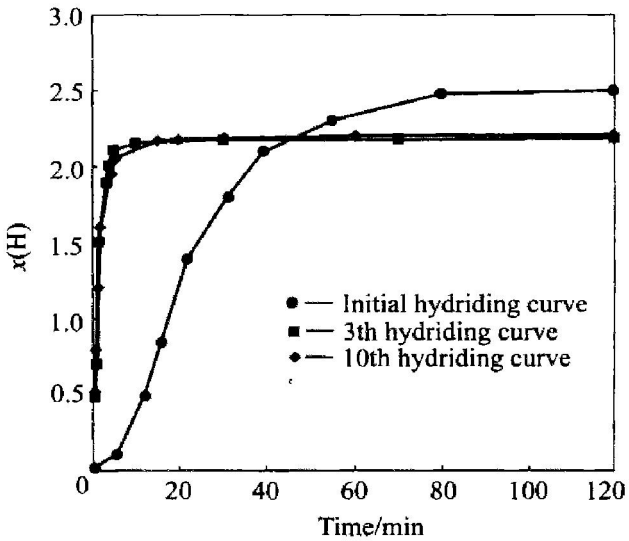

Fig. 2 Hydriding curves of $Ti_{1.2}Fe$+ 3% Mg alloys for various cycles at room temperature under 6.0 MPa

From the metallurgical micrograph of the alloys, as illustrated in Fig. 3, it can be found that some secondary phase is dispersed in the form of small-interlarded particles throughout the majority base phase of a network-like structure. As it is described later, SEM-EDS results showed the existence of such secondary phases with high Mg-rich. Both Mg particles and α-Ti phase in the matrix had the function to improve the activation properties of the alloys. As it is shown in the experiments, when the amount of Mg increased from 1% up to 3% and 5%, the initial hy-

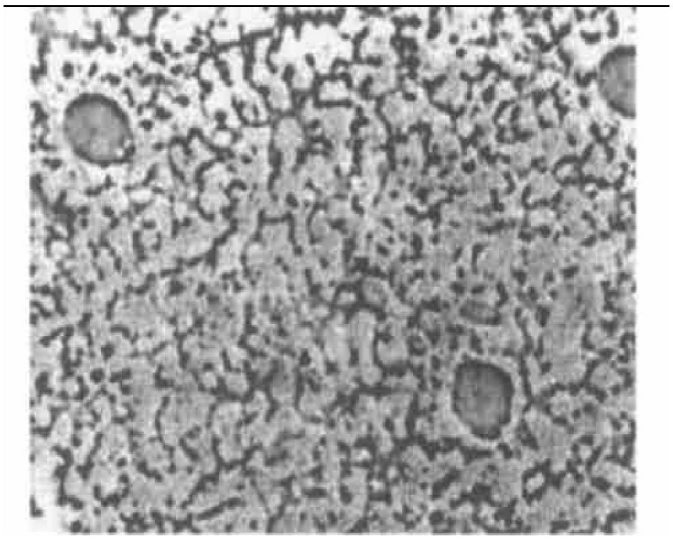

Fig. 3 Micrograph of $Ti_{1.2}Fe$+ 3% alloys synthesized by MA

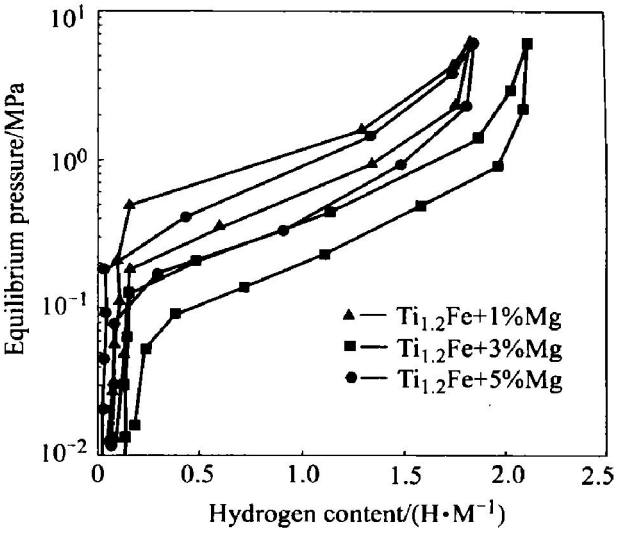

Fig. 4 Pressure-composition isotherms of $Ti_{1.2}Fe+ x$ Mg (x = 1%, 3%, 5%) alloys at 293 K

drogen absorption rate of the alloys was improved remarkably. It can be considered that the effect of Mg is stronger than that of α-Ti. The fact that the addition of Mg improves the activation properties of TiFe alloys can be understood because the low density Mg provides more new catalytic surfaces of TiFe phase and more hydrogen diffusion channels.

3.2 Hydrogen storage properties of $Ti_{1.2}Fe + x$ Mg (x = 1%, 3%, 5%) alloys

The pressure-composition isotherms of $Ti_{1.2}Fe+ x$ Mg (x = 1%, 2%, 3%) alloys at 293 K are shown in Fig. 4. Compared with the TiFe-H system that has two pressure plateaus, each sample in the figures has only one pressure plateau and the Mg addition increases the slope of the TiFe plateau and decreases its pressure hysteresis. Also as it is shown in Fig. 4, the effect of Mg additive quantity on P-C-T properties, thermodynamic properties and hydrogen storage capacities of TiFe alloys is remarkably high. At 293 K under 6.0 MPa the hydrogen storage capacities of $Ti_{1.2}Fe+ x$ Mg are 196 mL/g for x = 1%, 222 mL/g for x = 3% and 198 mL/g for x = 5%. Pressure-composition isotherms of $Ti_{1.2}Fe+$ 3% Mg alloys at 293, 313 and 333 K are shown in Fig. 5. It can be seen that the hydrogen storage capacities of the alloys decrease with the increase of the test temperature.

The thermodynamic parameters of the samples were calculated by means of the Van't Hoff equation $\ln p \propto 1/T$. The hysteresis factor (H_f) and slope of plateau (S_f) derived from the p-C-T curves are listed in Table 1. And the calculation points for the H_f and S_f of $Ti_{1.2}Fe+$ 3% Mg (MA) alloy, for example, are given as follow: $H_f = \ln (p_a/p_d)_{x(H)/x(M)=1.2}$, $S_f = (\ln p_{x(H)/x(M)=2.0})/(\ln P_{x(H)/x(M)=0.4})$. For comparison, the data for the classical TiFe alloy is also listed in Table 1. As it is described in Table 1,

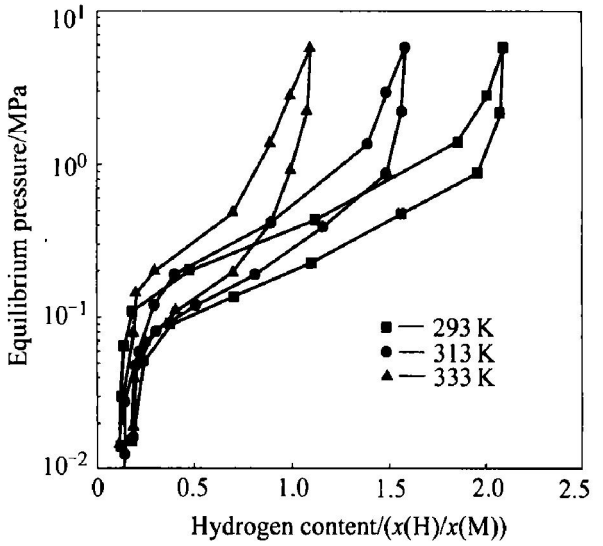

Fig. 5 Pressure-composition isotherms of $Ti_{1.2}Fe+$ 3% Mg alloys at 293, 313 (x(H)/x(M)) and 333 K

because of the addition of Mg and overstoichiometric Ti, all the $|\Delta H^{\ominus}|$ values for the three samples are clearly higher than that for TiFe, and the results are consistent with their lower hydrogen desorption pressure plateaus, comparing with TiFe's. The slopes of the samples' p-C-T plateau increased, however their hysteresis factor decreased obviously.

To clarify the effect of preparing methods as melting and MA on the properties of alloys, $Ti_{1.2}Fe+$ 3% Mg alloy as-cast was also prepared and its data were also measured and listed in Table 1. Both two $Ti_{1.2}Fe+$ 3% Mg samples showed similar thermodynamic data and p-C-T curves, except that the sample prepared by MA has a higher hydrogen storage capacity. Hydrogen storage capacities of as-cast alloys $Ti_{1.2}Fe+$ 1% Mg, $Ti_{1.2}Fe+$ 3% Mg and $Ti_{1.2}Fe+$ 5 % Mg are 185 mL/g, 213 mL/g and 190 mL/g, respectively.

Table 1 Properties of *P-C-T* curves and thermodynamics for experimental alloys

Synthesis method	Experimental alloys	Chemical formula	$-\Delta H^{\ominus}(H_2)$ /(kJ·mol^{-1})	$-\Delta S^{\ominus}$ /(J·K^{-1}·mol^{-1})	Hysteresis factor H_f	Slope of plateau S_f
Mechanical alloying	$Ti_{1.2}Fe$+ 1% Mg	$Ti_{1.2}FeMg_{0.04}$	40.8	119.6	0.43	1.42
	$Ti_{1.2}Fe$+ 3% Mg	$Ti_{1.2}FeMg_{0.12}$	38.1	117.5	0.49	1.53
	$Ti_{1.2}Fe$+ 5% Mg	$Ti_{1.2}FeMg_{0.20}$	39.3	119.4	0.56	1.64
As cast	$Ti_{1.2}Fe$+ 3% Mg	$Ti_{1.2}FeMg_{0.12}$	40.1	121.9	0.48	1.50
	TiFe[2]	TiFe	27.6	103.7	0.99	0

The results of the XRD analyses for the three samples prepared by MA are shown in Fig. 6. The results indicate that the main phase in the samples is TiFe phase and some $TiFe_2$ and α-Ti phases also exist in the alloys. The characteristic peak corresponding to the Mg element is too weak to be detected by XRD patterns. Also, from the XRD patterns, it was confirmed the existence of the weakest characteristic peaks of $TiFe_2$ phase and α-Ti phase in the $Ti_{1.2}Fe$+ 3% Mg alloy, which means that both the rates of $TiFe_2$ phase and α-Ti phase are low and in contrast to the high quantity TiFe phase. This is the reason why $Ti_{1.2}Fe$+ 3% Mg alloy has high hydrogen storage capacity. It is known that $TiFe_2$ phase is not a hydrogen storage phase and hydrogen absorbed in α-Ti phase cannot be desorbed at room temperature.

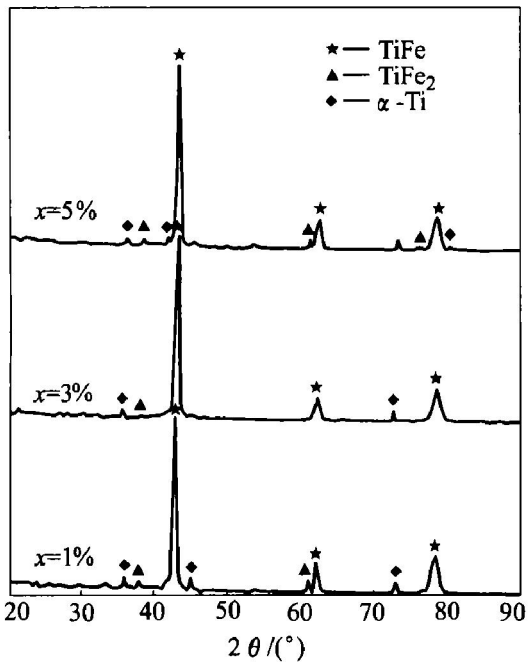

Fig. 6 XRD patterns of $Ti_{1.2}Fe$+ x Mg (x = 1%, 3%, 5%) alloys prepared by MA

The SEM micrograph of $Ti_{1.2}Fe$+ 3% Mg alloy prepared by MA is shown in Fig. 7. Systematically, EDS microanalysis within the scale for several tens microns was carried out. It turns out that there are three kinds of regions with different compositions as indicated in Table 2, whose mole ratios of region A and B are close to the mole ratio of TiFe and $TiFe_2$ and region C is Mg-rich region. EDS of the small regions about several tens microns shows that the regions with Ti: Fe mole ratio around 1: 1 dominate the entire sample. TiFe phase is the main phase in the samples prepared by MA. This is also fully consistent with the XRD results shown in Fig. 6. So, it can be concluded that the addition of Mg improves the hydrogen storage capacity of TiFe alloy by restraining the resultants of non-hydrogen-storage phase $TiFe_2$ and stable hydride phase α-Ti at room temperature in addition to improving the activation property of that alloy.

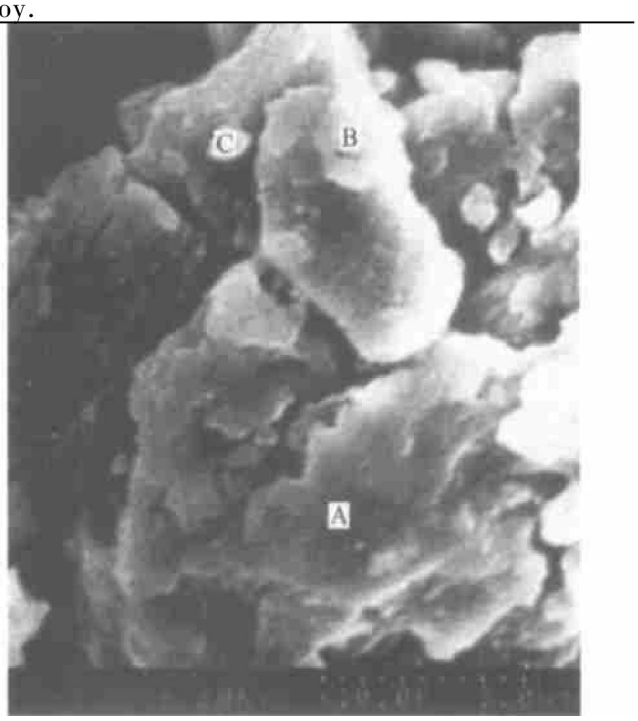

Fig. 7 SEM micrograph of $Ti_{1.2}Fe$+ 3% Mg alloy prepared by mechanical alloying

Table 2 Results of micro zone composition analysis of $Ti_{1.2}Fe$+ 3% Mg alloy by EDS (mole fraction, %)

Microzone	Ti	Fe	Mg
A	47.17	50.39	2.44
B	30.24	62.06	6.90
C	22.74	18.33	58.93

4 CONCLUSIONS

1) Mg-doped $Ti_{1.2}Fe$ alloys synthesized by Ti, Fe and Mg metal powders mixed and mechanically alloyed show good activation properties and can be fully activated in several hydriding/dehydriding cycles at room temperature. The reason that the addition of Mg and overstoichiometric Ti can markedly improve the activation properties of the alloys is believed to be due to the fact that Mg and α-Ti phase, which were easily dispersed throughout the TiFe base matrix, are hydrided prior to the hydrogenation of the TiFe matrix and then provide a further TiFe interface and hydrogen penetration path.

2) Among the three MA alloys, 3% Mg-doped alloy shows the best hydrogen storage properties. This alloy has a reversible hydrogen storage capacity of 222 mL/g and only one pressure plateau with a reduced pressure hysteresis. The addition of Mg can efficiently restrain the resultants of non-hydrogen-storage phase and room-temperature-stable hydride phase in the MA process, thereby it can retain the high hydrogen storage capacity of the alloy and simultaneously improve its activation properties.

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